NASA/TM—2000-210335

Cleaning of Fire Damaged Watercolor and Textiles Using Atomic Oxygen

Sharon K. Rutledge and Bruce A. Banks
Glenn Research Center, Cleveland, Ohio

Virgil A. Chichernea and Christy A. Haytas
Cleveland State University, Cleveland, Ohio

August 2000

The NASA STI Program Office . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized data bases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at ***http://www.sti.nasa.gov***

- E-mail your question via the Internet to help@sti.nasa.gov

- Fax your question to the NASA Access Help Desk at (301) 621-0134

- Telephone the NASA Access Help Desk at (301) 621-0390

- Write to:
  NASA Access Help Desk
  NASA Center for AeroSpace Information
  7121 Standard Drive
  Hanover, MD 21076

NASA/TM—2000-210335

Cleaning of Fire Damaged Watercolor and Textiles Using Atomic Oxygen

Sharon K. Rutledge and Bruce A. Banks
Glenn Research Center, Cleveland, Ohio

Virgil A. Chichernea and Christy A. Haytas
Cleveland State University, Cleveland, Ohio

Prepared for the
18th International Congress of the International Institute for Conservation
of Historic and Artistic Works
sponsored by the International Institute for Conservation
Melbourne, Australia, October 10–14, 2000

National Aeronautics and
Space Administration

Glenn Research Center

August 2000

Acknowledgments

The authors would like to give a special thanks to the Captain and crew of the Cleveland Fire Department Training Facility for all of their help with setting up and running the simulated arson fire.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076
Price Code: A03

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100
Price Code: A03

CLEANING OF FIRE DAMAGED WATERCOLOR AND TEXTILES USING ATOMIC OXYGEN

Sharon K. Rutledge and Bruce A. Banks
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Virgil A. Chichernea and Christy A. Haytas
Cleveland State University
Cleveland, Ohio 44115

SUMMARY

A noncontact technique is described that uses atomic oxygen generated under low pressure in the presence of nitrogen to remove soot from the surface of a test watercolor panel and strips of cotton, wool and silk. The process, which involves surface oxidation, permits control of the amount of surface material removed. The effectiveness of soot removal from test panels of six basic watercolors (alizarin crimson, burnt sienna, lemon yellow, yellow ochre, cerulean blue and ultramarine blue) and strips of colored cotton, wool and silk was measured using reflectance spectroscopy. The atomic oxygen removed soot effectively from the treated areas and enabled partial recovery of charred watercolors. However, overexposure can result in removal of sizing, bleaching, and weakening of the structure. With the proper precautions, atomic oxygen treatment appears to have great potential to salvage heavily smoke damaged artworks which were previously considered unrestorable.

INTRODUCTION

Fire in any structure housing an art collection can result in great cultural loss if the art is unrecoverable by conventional methods. Watercolor paintings on paper are particularly challenging to clean, especially when the damage is extensive and some charring of the paper has occurred. Textiles can also be difficult to treat when there has been soot accumulation. A noncontact treatment technique using atomic oxygen is usually able to selectively oxidize and remove soot and char leaving the pigment on the surface.

Research into using atomic oxygen as a treatment technique started as a result of enquiries made by the Conservation Department of the Cleveland Museum of Art as to available NASA technologies that could be used to remove urethane varnish. Presentation of the results and discussion with conservators from other organizations led to investigating the technique for removing soot and char from the surface of paintings and other fine art.

Atomic oxygen is present in the atmosphere surrounding the Earth at altitudes where satellites typically orbit. It has been shown to react chemically with polymers, surface coatings or deposits that contain carbon (ref. 1). In the reaction, the carbon is converted to carbon monoxide and some carbon dioxide. Water vapor can also be a by-product if hydrocarbons are present. This process can be harmful to a satellite if enough material is removed that is critical to its operation. Due to the importance of understanding the reaction, and the need to test potential solutions for protecting surfaces from reaction, facilities have been developed for producing atomic oxygen on Earth (ref. 3). Radio frequency (RF), microwave, and electron bombardment techniques have been used to dissociate molecular oxygen into atomic oxygen. These atoms can be either directed at the surface as a gentle flow of gas, or the surface can be immersed in the gaseous atomic oxygen. Exposure of large areas is typically performed in a vacuum chamber where pressures range from 0.001 to 100 mTorr, depending on the technique used. Smaller areas can be treated at atmospheric pressure using a DC arc device, as described in a publication by Banks, et al. (ref. 3). Because the process is dry and the reaction is confined to the surface, there is less risk of damaging the underlying paper or fabric structure.

The atomic oxygen cleaning technique has been demonstrated to be effective at removing soot from canvas, acrylic ‘gesso’, unvarnished oil paint and varnished oil paint (refs. 4 to 6). This paper investigates its usefulness in treating watercolors and textiles. The process, which has been patented by NASA, is not intended to be a replacement for conventional restoration techniques, but to be an additional tool for use where conventional techniques may not be effective (ref. 7).

PROCEDURE

Description of the Test Samples

Stripes of six basic watercolors in the Cotman series manufactured by Winsor & Newton (alizarin crimson, burnt sienna, lemon yellow, yellow ochre, cerulean blue and ultramarine blue) were applied to half a sheet of standard watercolor paper (medium weight acid free manufactured by Bienfang). The stripes were made wide enough (~2.54 cm) to allow measurement of reflected light from the surface of each individual watercolor. On the other half of the paper, a landscape was painted in order to determine what would occur during the treatment of mixed pigments.

The textile samples consisted of ~7 by 14 cm sections cut from 100 percent cotton (red and white flag stripe), 100 percent wool (blue and magenta houndstooth) and 100 percent silk (floral print). Patterns were selected to be as uniform as possible over a 2.54 cm diameter area to allow greater accuracy in measurement of the reflected light from the surface.

Smoke Exposure and Charring

Smoke exposure of the test samples was performed at the Cleveland Fire Department Training Facility. The training facility consists of a two-story building with corrugated metal outer walls and firewall separating rooms inside. At one end of one of these rooms a fire was produced in a stack of mattresses soaked with an accelerant solvent to simulate an arson fire. The test samples were placed at the other end of the room. Two ‘burns’ were performed. During the first ‘burn’, the fire flashed over to the test samples that were suspended by binder clips from nails on the wall opposite the fire. The watercolor experienced heavy thermal damage and charring. Most of the textiles were lost because they had been converted to ash. A second set of test samples was then prepared and this time placed inside of a stainless steel enclosure with a pulley operated door that could be raised if the temperature of the samples, as monitored remotely by a thermocouple inside the enclosure, became too high. A tubing connection was made from the enclosure to an air compressor that provided cool air to lower the temperature inside the enclosure. The second ‘burn’ resulted in samples that received a soot accumulation without the thermal damage. Both watercolors from ‘burns’ one and two as well as the textiles from ‘burn’ two were used to test the atomic oxygen treatment process.

Atomic Oxygen Cleaning

Cleaning of the test samples was performed inside a large vacuum chamber that can accommodate paintings or textiles of ~1.5 by 2.1 m in size, suspended in a vertical position. In the chamber the vacuum is produced by conventional mechanical roughing and blower pumps with pressures during treatment which range from 1 to 5 mTorr. There is potential for dehydration shrinkage to occur during the treatment process due to the fact that it is performed under a partial vacuum. To date, none of the materials treated have experienced any cracking, tearing, or other signs of damage due to exposure to a partial vacuum (refs. 4 to 6). This may not be the case for every material combination, and a risk assessment should be made prior to treatment in order to determine if the shrinkage of the base material, medium, and stretcher are sufficiently matched to prevent cracking or tearing. This technique has been typically used to restore severely damaged works of art, so the benefit of being able to salvage it has been much greater than the risk of shrinkage.

Two large aluminum parallel plates inside the chamber are used as electrodes to create the atomic oxygen through RF excitation. One plate is connected to a radio frequency power supply manufactured by RF Power Products Inc. operating at 400 W, while the other plate is at ground potential. The ground plate has several bolts attached to it from which works of art to be cleaned can be suspended. The test samples were mounted onto a commercially available artist's stretched canvas by hanging them from binder clips suspended on paper clips pushed through the canvas. Half of each sample was left untreated by covering it with a polymer sheet (polyimide, Kapton) held in close contact to prevent atomic oxygen from reaching the surface of the sample. A controlled entry of air into the chamber at rates between about 130 and 280 standard cubic centimeters per minute provided the source of the oxygen. The RF (13.56 MHz) oscillating voltage between the two metal plates causes dissociation of the molecular oxygen and nitrogen in the air into atomic species, creating a plasma discharge between the plates which has a pink glow. The nitrogen in the air has been found to have no effect on the artwork or on the removal rate of carbon and behaves as an inert gas in the exposure treatment. An automated timer and NASA designed and constructed controller on the system allows the cleaning to proceed unattended over a desired duration and will turn off the system if a loss in vacuum, water cooling to the pumps and power supply, or drop in plasma intensity is detected.

Additional samples of each type of watercolor, which had been painted onto separate pieces of watercolor paper and not exposed to smoke, were treated with atomic oxygen in a smaller but very similar RF system (Plasma Prep II manufactured by Structure Probe Inc.). This testing was performed in order to determine how quickly watercolors bleach once atomic oxygen reaches the pigment. This system also produces atomic oxygen from air but operates at 100 W of RF power. Samples were placed on glass slides to prevent atomic oxygen from reaching the reverse side of the paper. The enclosure that the samples were placed in for treatment is 10.5 cm in diameter by 15 cm long. The pressure in the chamber during exposure was ~50 to 200 mTorr. Atomic oxygen arrival was at a rate similar to that in the larger facility. The Kapton equivalent atomic oxygen arrival flux in both facilities was $\sim 3.5 \times 10^{15}$ atoms/cm^2-sec.

Analysis

A Laboratory Portable Spectro-Reflectometer (LPSR) manufactured by AZ Technologies was used to measure the light reflected from the surface of the samples as a function of wavelength between 250 and 2500 nm. The data could then be compared in the visible region as a function of wavelength between 400 and 700 nm. Data were also normalized with respect to the human eye response (visibility curve) (ref. 8) to give a single value of reflectance that represents the region of the spectrum where the eye is most sensitive.

RESULTS AND DISCUSSION

Watercolors

The watercolor from 'burn' number 1 received extensive damage. Portions were missing and the paper appeared a dark grey through its' thickness. The brittle nature of the paper can be seen by the cracking shown in the lower right of figure 1(b) in comparison to a photo of the original watercolor prior to the fire exposure in figure 1(a). Figure 1(c) shows the same watercolor after treatment with atomic oxygen for ~2.5 hr. After treatment, much more of the detail of individual stripes on the left and the details of the tree on the far right are visible. The color could not be restored completely due to thermal damage to the paper that cannot be reversed.

The watercolor from 'burn' number 2 received only soot on the surface. The lack of thermal damage made it easier to determine if the treatment process would cause changes in pigment coloration. Reflectance measurements were made from each watercolor stripe prior to smoke exposure, after smoke exposure, and after smoke exposure followed by atomic oxygen treatment for ~7 hr. After treatment, the reflectance for burnt sienna and yellow ochre returned to levels very close to their original values measured before exposure to the simulated arson fire. The total reflectance as a function of wavelength for burnt sienna prior to smoke exposure, after smoke exposure, and after smoke exposure followed by atomic oxygen treatment is shown in figure 2(a). Alizarin crimson and lemon yellow experienced slight bleaching, indicated by an increase in reflectance after treatment in comparison to the original watercolor. Ultramarine blue became very slightly redder. The greatest change was for the cerulean blue watercolor, which experienced a green shift due to the treatment process. The reflectance data for this watercolor is shown in figure 2(b).

Further exposures were performed on watercolors that had not received smoke exposure in order to determine how quickly bleaching or darkening occurs once the surface of the paint is reached, and whether the change is limited or continues to occur as treatment time progresses. The reflectance normalized with respect to the eye's visual response was monitored at different times during the treatment of the six watercolors. The burnt sienna, lemon yellow and ultramarine blue changed very little with treatment during the time they were exposed (up to ~135 min). The yellow ochre showed a slight lightening after about 60 min of exposure. Alizarin crimson showed a continued slight bleaching as treatment progressed. The cerulean blue experienced the most change with exposure. The data are summarized in figure 3. The landscape scene regained its detail and sharpness after atomic oxygen treatment. The coloration was slightly lighter in areas where pigments were used that were shown to experience bleaching with treatment. The results indicate that, for some pigments, it is important to minimize the time that the pigment is exposed to atomic oxygen once the soot has been removed from the surface to prevent bleaching or changes in coloration.

Textiles

Smoke exposed textiles from 'burn' number two were also half covered with a polymer sheet (Kapton polyimide) prior to atomic oxygen treatment in order to preserve one side as a control. Figure 4 shows the textiles after atomic oxygen treatment for 6.25 hr. The treated sections of the cotton, wool and silk are facing toward the center of the photograph. The treatment removed most of the soot from the surface and restored the coloration of the wool and silk, but there was a slight bleaching of the red cotton after exposure. The white cotton stripe in the fabric was not fully cleaned by treatment for this length of time (figs. 5(a) and (b)). If treatment continues too long, the fabric will be weakened by thinning of the cellulosic fibers; therefore there is a trade-off between fully removing the soot and having an unbleached, strong fabric. With careful control of the treatment time, most of the soot could be removed safely from the surface of the cotton, wool and silk.

Cautions

Caution must be used when treating an untested pigment or textile using atomic oxygen. A representative edge or corner which is typical of the whole should be tested first with the remainder masked off, so that a determination can be made if the process will be safe for the pigments or dyestuffs present. Some watercolors will undergo bleaching as treatment progresses and care must be taken to restrict the treatment time so that changes in coloration can be limited. Organic fibers and organic pigments can also be removed with overtreatment. As more testing occurs, a greater knowledge base will be developed regarding the types of materials that can or cannot be treated using this technique.

CONCLUSIONS

Atomic oxygen appears to have great potential for removing soot and char from the surface of art damaged during a fire, and may be able to allow the recovery of works of art previously believed to be unrestorable. The process is not intended to be a replacement for conventional techniques, but as an additional conservation tool in applications where conventional techniques have not been effective.

REFERENCES

1. Banks, B.A. and Rutledge, S.K., "Low Earth Orbital Atomic Oxygen Simulation for Materials Durability Evaluation," *Proceedings of the Fourth European Symposium on Spacecraft Materials in the Space Environment,* CERT, Toulouse, France, Sept. 6–9, (1988), 371–392.
2. Banks, B.A., Rutledge, S.K., Paulsen, P.E., and Stueber, T.J., "Simulation of Low Earth Orbital Atomic Oxygen Interaction with Materials by Means of an Oxygen Ion Beam," *Presented at the 18th Annual Symposium on Applied Vacuum Science and Technology,* (1989), NASA TM–101971.
3. Banks, B.A., Rutledge, S.K., and Norris, M.J., "An Atmospheric Atomic Oxygen Source for Cleaning Smoke Damaged Art Objects," *Presented at the 26th Annual AIC Meeting,* Arlington, VA, June 1–7, (1998), NASA/TM—1998-208506.
4. Rutledge, S.K. and Banks, B.A., "Atomic Oxygen Treatment Technique for Removal of Smoke Damage from Paintings," *Presented at the Materials Research Society Meeting,* Boston, MA, December (1996), NASA TM–107403.
5. Rutledge, S.K., Banks B.A., Forkapa, M.J., Stueber, T.J., Sechkar, E.A., and Malinowski, K., "Atomic Oxygen Treatment as a Method of Recovering Smoke Damaged Paintings," *Presented at the 26th Annual AIC Meeting,* Arlington, VA, June 1–7, (1998), NASA/TM—1998-208507.
6. Rutledge, S.K., Banks, B.A., and Chichernea, V.A., "Recovery of a Charred Painting Using Atomic Oxygen Treatment," *Proceedings of the 12th Triennial Meeting of the International Committee for Conservation, ICOM*, Lyon, France, August 29–Sept. 4, (1999), NASA/TM—1999-209435, pp. 330–335.
7. U.S. Patent #5,560,781: Banks, B.A., and Rutledge, S.K., *Process for Non-Contact Removal of Organic Coatings from the Surface of Paintings,* (1996).
8. Koller, L.R. *Ultraviolet Radiation* 2nd Edition, John Wiley & Sons, New York (1965), pp. 6–7.

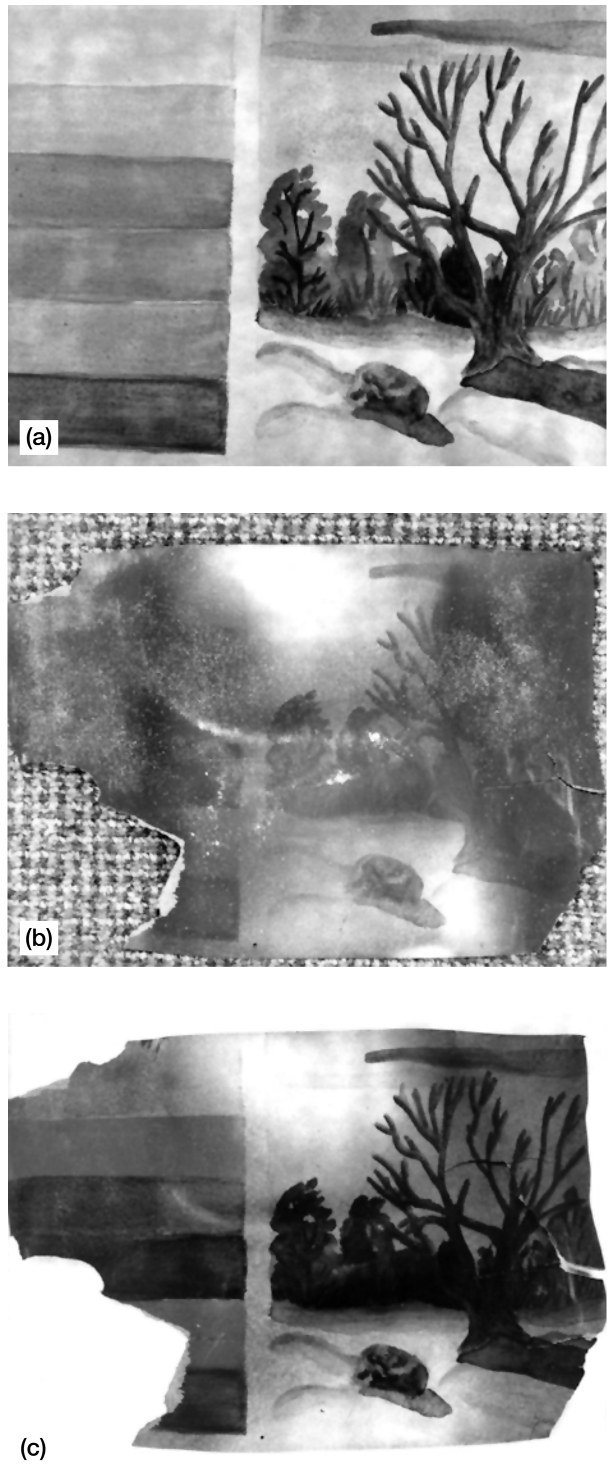

Figure 1.—Watercolor on watercolor paper (test panel). (a) Prior to 'burn' 1 at the Cleveland Fire Department. (b) After 'burn' 1. (c) After atomic oxygen treatment for 2.5 hours.

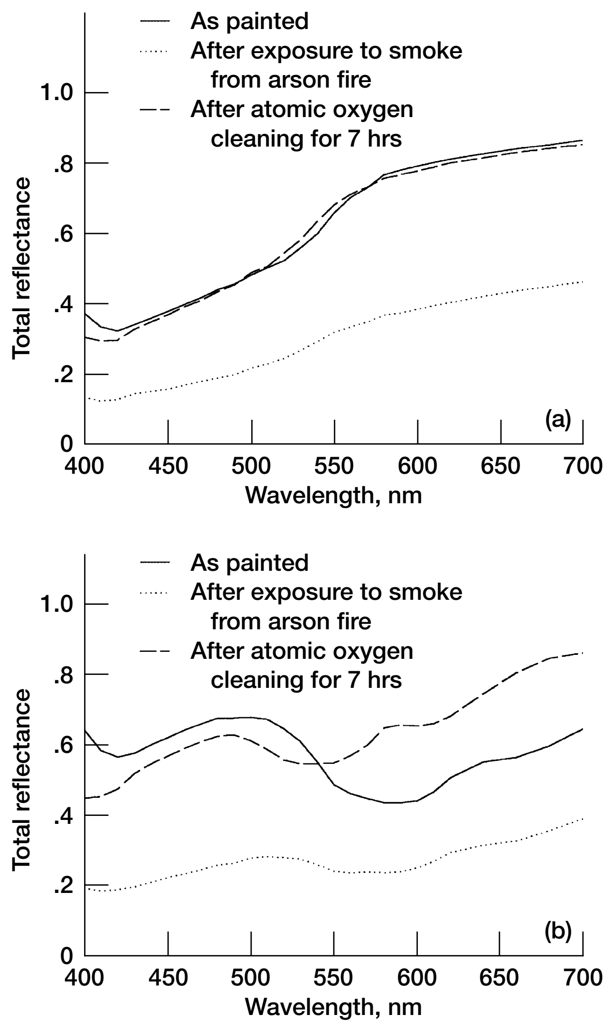

Figure 2.—Reflectance as painted, with smoke exposure and after atomic oxygen treatment for 7 hours. (a) Burnt sienna watercolor. (b) Cerulean blue watercolor.

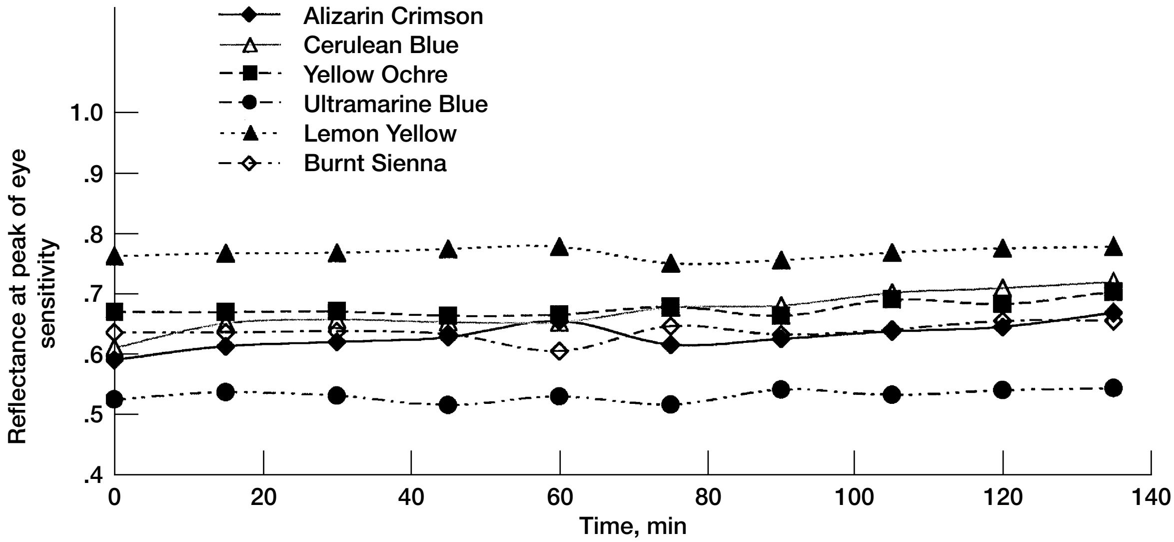

Figure 3.—Total reflectance at the peak of the eye sensitivity (550 nm) for the pristine pigmented surface of the six different watercolors as a function of atomic oxygen exposure duration.

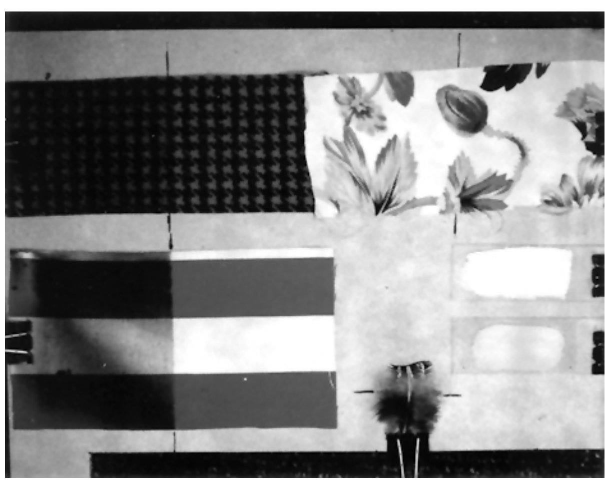

Figure 4.—Photograph of smoke exposed textiles after treatment of the central half of each with atomic oxygen.

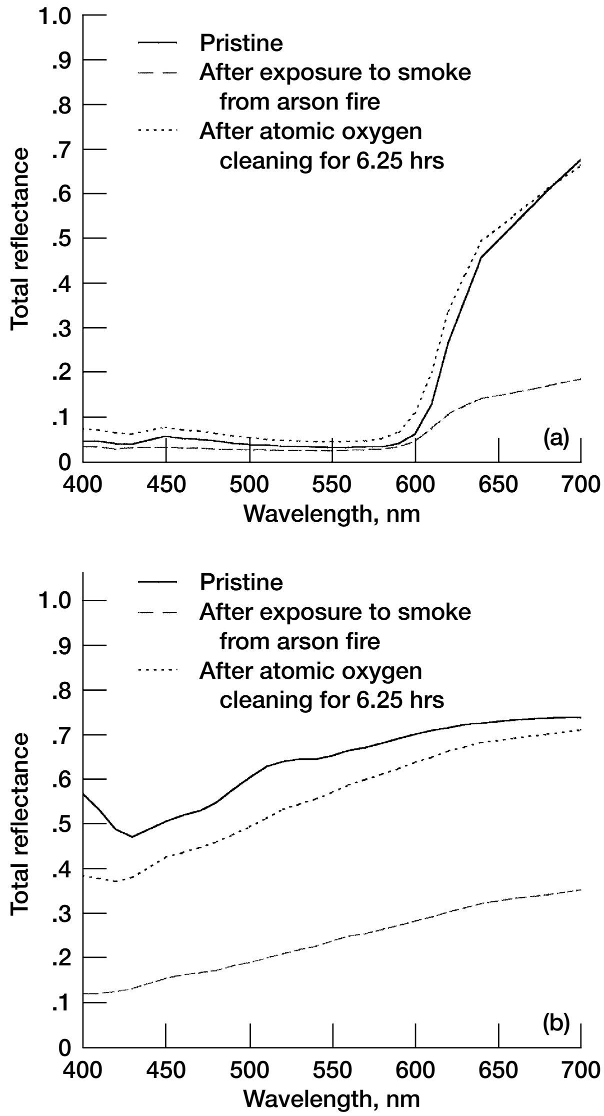

Figure 5.—Total reflectance as a function of wavelength for samples pristine, with smoke exposure and after atomic oxygen treatment for 6.25 hours. (a) Red cotton. (b) White cotton.

REPORT DOCUMENTATION PAGE	*Form Approved OMB No. 0704-0188*

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	August 2000	Technical Memorandum

4. TITLE AND SUBTITLE

Cleaning of Fire Damaged Watercolor and Textiles Using Atomic Oxygen

5. FUNDING NUMBERS

WU–251–30–1E–00

6. AUTHOR(S)

Sharon K. Rutledge, Bruce A. Banks, Virgil A. Chichernea, and Christy A. Haytas

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E–12379

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM—2000-210335

11. SUPPLEMENTARY NOTES

Prepared for the 18th International Congress of the International Institute for Conservation of Historic and Artistic Works sponsored by the International Institute for Conservation, Melbourne, Australia, October 10–14, 2000. Sharon K. Rutledge and Bruce A. Banks, NASA Glenn Research Center; Virgil A. Chichernea and Christy A. Haytas, Cleveland State University, 983 E. 24th Street, Cleveland, Ohio 44115–2403. Responsible person, Sharon K. Rutledge, organization code 5480, (216) 433–2219.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category: 27 Distribution: Nonstandard

This publication is available from the NASA Center for AeroSpace Information, (301) 621–0390.

12b. DISTRIBUTION CODE

13. ABSTRACT ***(Maximum 200 words)***

A noncontact technique is described that uses atomic oxygen generated under low pressure in the presence of nitrogen to remove soot from the surface of a test watercolor panel and strips of cotton, wool and silk. The process, which involves surface oxidation, permits control of the amount of surface material removed. The effectiveness of soot removal from test panels of six basic watercolors (alizarin crimson, burnt sienna, lemon yellow, yellow ochre, cerulean blue and ultramarine blue) and strips of colored cotton, wool and silk was measured using reflectance spectroscopy. The atomic oxygen removed soot effectively from the treated areas and enabled partial recovery of charred watercolors. However, overexposure can result in removal of sizing, bleaching, and weakening of the structure. With the proper precautions, atomic oxygen treatment appears to have great potential to salvage heavily smoke damaged artworks which were previously considered unrestorable.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Atomic oxygen; Art restoration; Treatment	15
	16. PRICE CODE
	A03

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	